SINGLE CRYSTAL GROWTH FROM MELT UNDER SPACE ENVIRONMENT

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ABSTRACT

A brief outline of the methods of single crystal growth from melt under 1-g is presented and their relative merits discussed. The role of near 0-g environment and other practical parameters important to the growth of perfect single crystals is considered. The effect of interface shape, high-g, gamma-ray irradiation and electromagnetic body force is reviewed. The experiment to study the growth kinetics under various equivalent gravity fields is discussed in more general terms and a partial list of the candidate materials suitable for space crystal growth is presented.

INTRODUCTION

The age of solid state electronics was inaugurated by the large scale availability of highly pure and superior quality single crystals of germanium and silicon. The crystal growth, in return, has been vastly benefited by the availability of sophisticated control electronics. Definite improvements of the crystal quality in purity and crystalline perfection has been attained. A new era, i.e., SPACE AGE, was launched a decade ago. We have reached the point now to seriously consider the industrial usage of the "space". This conference on space processing is a step in this direction; to seek and establish a true dynamic equilibrium between man⇄space and also between technical utilization⇄fundamental research. A vast laboratory containing hard vacuum, radiation flux and near zero-gravitational body force is available to experiment. It seems possible that under space environment, large size

single crystals of higher perfection can be grown. My talk will confine itself to the problems of melt crystal growth.

Growing single crystals in space ought to be viewed as a unit step towards understanding many complex space processing problems. A single crystal grown from the melt is a result of controlled solidification as contrasted to casting, which is purposely uncontrolled. Proper understanding of the dynamics of solid/liquid interface in near 0-g will not only assist in growing dislocation-free, optical quality laser and maser materials, but will also present insight into whether a perfect ball bearing can be manufactured. I plan to discuss the following topics. Their relevance to space processing will be pointed out at the proper places.

A. Why 0-g crystal growth from the melt?
B. Which technique is most suited for space experiment and why?
C. What is the influence of growth parameters on crystal perfection?
D. What is the effect of electromagnetic body force and radiation on crystal growth?
E. How does the interface shape affect crystal perfection?
F. Does high-g affect crystal size and perfection?
G. How to study 0-g effects on earth (the crucial experiment)?
H. What materials are suitable for space processing?

A. Fig. 1 compares the magnitude of the interatomic forces of the solid matter, liquid matter, surface tension force and the 1-g gravitational body force (mg, m = 1 gm). The g-force will have negligible effect on the solid state processes since the cohesive force of the solid matter, and also the energy required for most solid state reactions (self-diffusion, phase-change, precipitation), are 10^{8}-10^{9} times greater than g itself. However, the solid/liquid interfacial tension and the cohesive force of the liquid matter fall within the magnitude regime of g and, therefore, considerable interaction is possible.[1] To grow single crystals from the melt or liquid state in a near 0-g environment is, thus, an interesting proposition.

B. Some of the common techniques of single crystal growth from melt are: (a) Czochralski (1918), (b) zone-melting (1952), (c) Bridgeman, (d) Verneuil (1890), (e) flux, (f) hydrothermal, and (g) solution growth. Although the last of the three techniques can yield good optical quality single crystals, the crystal size is generally very small. In addition, they require an extensive knowledge of the phase equilibrium in the multi-component system.[2] The first four, a to d, are the most commercially used techniques. Details of these techniques are given in recent monograph[3] and in a review paper.[4]

(a) The Czochralski Technique

This technique of pulling from the melt is the preferred method for obtaining large

single crystals. A seed crystal is dipped into the melt and gradually withdrawn. Before growth can start, the thermal equilibrium at the melt/solid interface needs to be established and the provision has to be made so that the latent heat of fusion is removed from the interface. Some advantages of this technique are: (1) The crystal need never be touched; (2) control of orientation is easy; (3) the diameter of the crystal can be easily varied; (4) the crystal is cooled without external mechanical restraints. Dislocation-free single crystals of Ge, Si and such metals as Al have been grown. Nassau and Broyer[5] have discussed the criteria for the Czochralski technique. The ideal materials suitable for growth by this technique would have the following properties: (1) congruent melting point, (2) no destructive phase change, (3) low vapor pressure, (4) low viscosity, (5) suitable growth habit, and (6) suitable crucible must be available.

(b) The Floating Zone Technique:

In this technique, a thin molten layer of the material traverses through the body of the solid matter.[6] The technique is suited for high melting point materials (above 2000°C). Since no crucible is used, the problem of crucible contamination is eliminated. The strains due to differential expansion of the crucible and the crystal is absent. One shortcoming of the technique is the limitation on zone length,

$$Lm \simeq 2.8\sqrt{\frac{\gamma}{\rho g}} \quad \text{——— (Heywang's relation).}^{7}$$

Where Lm is the limiting maximum zone height, ρ denotes density, γ, the surface tension, and g, the gravity. Under near 0-g, Lm will be quite large, a decisive advantage of space processing. It is also difficult to obtain a proper temperature distribution. A large radial gradient usually encountered in the system gives rise to high dislocation densities.[3]

(c) The Bridgeman Technique :

The melt in a container is moved relative to a fixed temperature gradient.[4] The technique is suitable for low melting point materials. Generally, the dislocation density of the grown crystal is high.

(d) The Verneuil Technique (1890):

Large single crystals of saphire and ruby have been grown by the Verneuil or flame fusion technique. The technique may be considered to be an inverted arrangement of the Czochralski method,[8] where a liquid layer is continuously replenished. The crystal quality is moderate due to severe temperature gradient and highly localized heat source at the interface. The numerous disadvantages of this technique are: (1) highly strained single crystals, (2) chemical inhomogeneity--a serious problem

for laser materials, (3) high dislocation density and subgrain structure, and (4) contain index of refraction variation which affect the optical path of the crystal. For laser and maser applications, these inhomogeneity and imperfections lead to high optical losses, broad emission line widths and warping of the amplified light wavefronts. The advantage of the technique, however, is fast growth of large size crystals. At this stage, the Czochralski technique appears most suited for 0-g crystal growth. The crystal puller essentially consists of a crucible to hold the melt, a seed with known crystallographic orientation, a means of heating the melt, a mechanism for producing relative motion of the seed and melt and, if needed, provision for special atmosphere (see Fig. 2).

C. The crystal perfection depends on the critical control of the growth parameters, viz., the melt temperature, growth rate, diameter of the crystal and on the thermal gradient at the interface. Usually a compromise between the crystal quality and the ultimate size of the crystal, which depends on the growth rate and the thermal gradient, has to be made. Figures 3 to 5 illustrate this point. Higher growth rate, increased axial temperature gradient and larger diameter result in higher density of grown-in dislocations.[9,10] Since these line defects do not exist in thermodynamic equilibrium, they are difficult to eliminate by post-annealing treatments. Maximum diameter of dislocation-free Al single crystal grown is 0.3mm only.[9] Existing techniques have not lent themselves to grow a larger diameter metallic single crystal. The near 0-g crystal growth might be the answer.

The melt in the crucible experiences free thermal convection induced by gravity. Turbulent flow or overstability results if Rayleigh number Ra, which is a dimensionless parameter, exceeds a certain critical value ($\simeq 1700$). The Rayleigh number, Ra, is a product of the Grashof Gr and Prandtl Pr number.[11]

$$Ra = \left[\frac{g\beta \Delta T L^3}{\nu^2}\right] \left(\frac{Cp\mu}{k}\right) = Gr.\ Pr\ .$$

Where β = volume coefficient of thermal expansion
g = acceleration of gravity
ΔT = temperature difference across L
L = characteristic dimension of the system (length, height, diameter)
ν = kinematic fluid viscosity
μ = absolute fluid viscosity
Cp = specific heat at constant pressure
k = thermal conductivity.

In the case of metals, for reasonable choice of L and ΔT, Ra exceeds 10^5. It is certain from the above relation that under near 0-g, Ra will be greatly reduced and, thus, a large size, perfect single crystal of metals can be grown. A good sized dislocation-free single crystal of elemental and compound semiconductors has been

prepared on earth. It is thought that either they have a large Peirl's stress[12] or the intrinsic strength of the crystal exceeds the thermal and chemical stress close to the melting point.[13]

Seed Rotation:

This is provided to overcome the thermal asymmetry of the melt. An optimum rotation rate is desired for best results.

Chemical Inhomogeneity--Banding:

These are observed in the melt-grown alloy or compound single crystals. Generally, the solutes or impurities have different solubilities in the solid and in the liquid. Fig. 6 illustrates this fact schematically. The equilibrium distribution coefficient K_o is defined as the ratio C_S/C_L and is <1 or >1, depending on the binary phase diagram; but in most practical cases it is <1.

During crystal growth, as solidification proceeds, the solute is rejected at the interface and builds up an enriched diffusion layer.[14] Fig. 7 describes this situation on a composition distance plot. The thickness of the diffusion boundary layer is equal to D/V (diffusion distance, δ) where D is the solute diffusion in the liquid and V is the growth rate. Superimposed to this boundary layer, if a thermal convection exists (g-induced), then solute banding parallel to the interface is observed. These are two dimensional imperfections perpendicular to the growth axis which appear as striations. In laser crystals, they cause scattering of a laser beam and seriously impair the usefulness of crystals. Solute banding can be reduced by decreasing the thickness of the diffusion boundary layer or by eliminating thermal fluctuation on the interface. The second will be easier to achieve in the absence of gravity. The enhanced impurity concentration at the growing interface can also cause the interface shape to change from planar to a cellular form. Fig. 8 illustrates how to suppress constitutional supercooling which results in cellular structures and preferred growth directions in the crystals. High growth rates and sharp temperature gradient are required to avoid constitutional superconducting, which are in direct conflict to grow dislocation-free single crystals.[4]

D. Johnson and Tiller[15] have experimentally studied the effect of electromagnetic body force on δ and have shown the functional relationship,

$$\frac{\delta}{D_L} = B \exp(-mH^2) .$$

Where H = magnetic field, B, m = constant for the system. Higher H reduces the thickness, δ. Further work of Harvey and Utech[16] and M. Schieber[17] indicates that the solute banding is suppressed and also the thermal fluctuations damps out by the application of magnetic field.

Radiation:

G. D. Botsaris, et al[18], studied the effect of gamma-radiation on growth of KCL single crystals grown from aqueous solution. The dislocation density was reduced when the growth took place in a radiation field. The changes in equilibrium surface structure of crystals (KDP) grown under gamma-irradiation was investigated by C. Motoc.[19] It was concluded that the presence of irradiation is equivalent to growth in the presence of impurities. The factor of irradiation must be considered in any space processing.

E. Shape of the solid/liquid interface is an important parameter which determines the uniformity in thermal gradient and the pulling rate.[20] A planar interface is sought in order to grow a perfect crystal. A shape convex to the melt is the most common and is acceptable. The recent use of afterheaters,which are placed directly above the melt and surround the growing crystal, have resulted in production of low dislocation density compounds. The equilibrium shape of the interface in the absence of gravity will be dictated by surface tension force and will assume a hemispherical shape. This can be shown by the treatment of Beliustin.[21] The height-to-width ratio (h/w) of an interface is given by,

$$\frac{h}{w} = \frac{Bw}{w+Av} \quad .$$

Where $B \simeq \frac{1}{2}$; $A = \frac{g(\rho_1 - \rho_2)}{4\sigma_{12}}$,

σ_{12} = surface energy per unit area at the crystal-solution interface,
ρ_1, ρ_2 = density of the crystal and the solution,
v = volume of the crystal.
Therefore, at g = 0, h/w = 1/2 = hemisphere. There might arise the problem of seed wetting, which, however, can be achieved either by changing the equilibrium interface shape by the use of afterheaters or by intentional impurities.

F. Effect of High-g on Crystal Perfection:

The preliminary results on the influence of high-g on solution crystal growth has been published by Schlichta and Knox.[22] The solution was rotated in a centrifuge. Higher g caused super saturation and, hence, crystal growth. The crystal size became smaller at higher g ($\simeq$ 40,000 g) and showed extensive strain damage due to high force fields. A brief review of the practical aspect of growing perfect single crystals was presented.

Let me discuss now the crucial experiments that we are planning to undertake, which should demonstrate the feasibility and practicality of 0-g crystal growth. Planned, is a single crystal growth of a ferro- or a ferri-magnetic compound under

an electromagnetic body force. On earth, the 0-g environment cannot be achieved over an extended period by the drop tower, or the airplane trajectory technique. The magnetic method, on the other hand, can provide a range of gravities including near 0-g for longer duration. Two possibilities exist. In one, the melt is placed in a magnetic gradient and the magnetic force is adjusted to counteract all or part of the g-body force. The second technique has been adequately described by Kirk.[11,23]

G. The experiment will consist of the crucible containing the melt with two electrodes on two sides so that a current is passed horizontally. The magnetic field line will superimpose also horizontally but normal to the current flux. The electric current density will interact with a component of the magnetic field transverse to it and yield a body force normal to the current-magnetic field plane. Fig. 9 illustrates the proposed experiment. The attention, however, has to be paid to the sources of error and the interferring effects of the impressed magnetic and electric field, for example, joule heating, galvanomagnetic and thermomagnetic effects. The equivalent gravities, according to Kirk, is given by a simple expression,

$$\frac{g^*}{g_c} = \sigma_e \frac{(\overline{J} \times \overline{B})}{\alpha \rho_o g_c} \quad .$$

Where g^* = equivalent gravitational acceleration produced by the imposed electromagnetic body force, $\frac{\text{meters}}{\text{sec}^2}$,

g_c = the earth's sea level acceleration, $\frac{\text{meter}}{\text{sec}^2}$,

$\overline{J}$ = electric current density, $\frac{\text{amperes}}{\text{meter}^2}$,

$\overline{B}$ = magnetic flux density, $\frac{\text{webers}}{\text{meter}^2}$,

$\sigma_e = \frac{\delta \sigma}{\sigma_o \delta T}$ = temperature coefficient for electrical conductivity charge, $^{o}k^{-1}$,

α = coefficient of volume expansion $= \frac{\delta \rho}{\rho_o \delta T}$, $^{o}k^{-1}$,

ρ_o = mass density, $\frac{\text{kg}}{\text{meter}^3}$.

Although conceptually the problem is straightforward, experimentally it is quite complex. Magnets with pole-gaps larger than 2 3/4 inches are not available to us. The crystal growth assembly including all essential parts has to be fitted in this small gap.

H. Finally, I would like to make some general comments regarding the materials to be suitable for space crystal growth. The fundamental research and the technological utilization should be considered jointly. Also, the basic attributes of space environment must be understood. For example, the selection of a congruently melting material which has a low vapor pressure takes into account the hard vacuum of

space. Table 1 lists some of the candidate materials. The listing is by no means complete. GaAs and $LiNbO_3$ single crystals are already available in large quantities. They will serve a good example to learn and acquaint oneself with the preparation of perfect single crystals. The near 0-g environment might also affect the preparation of the organic superconductors proposed by Little[24] about five years ago. Vast sums of money and effort have gone into the synthesis of this one-dimensional, room-temperature superconducting material without success. Space processing may be the answer.

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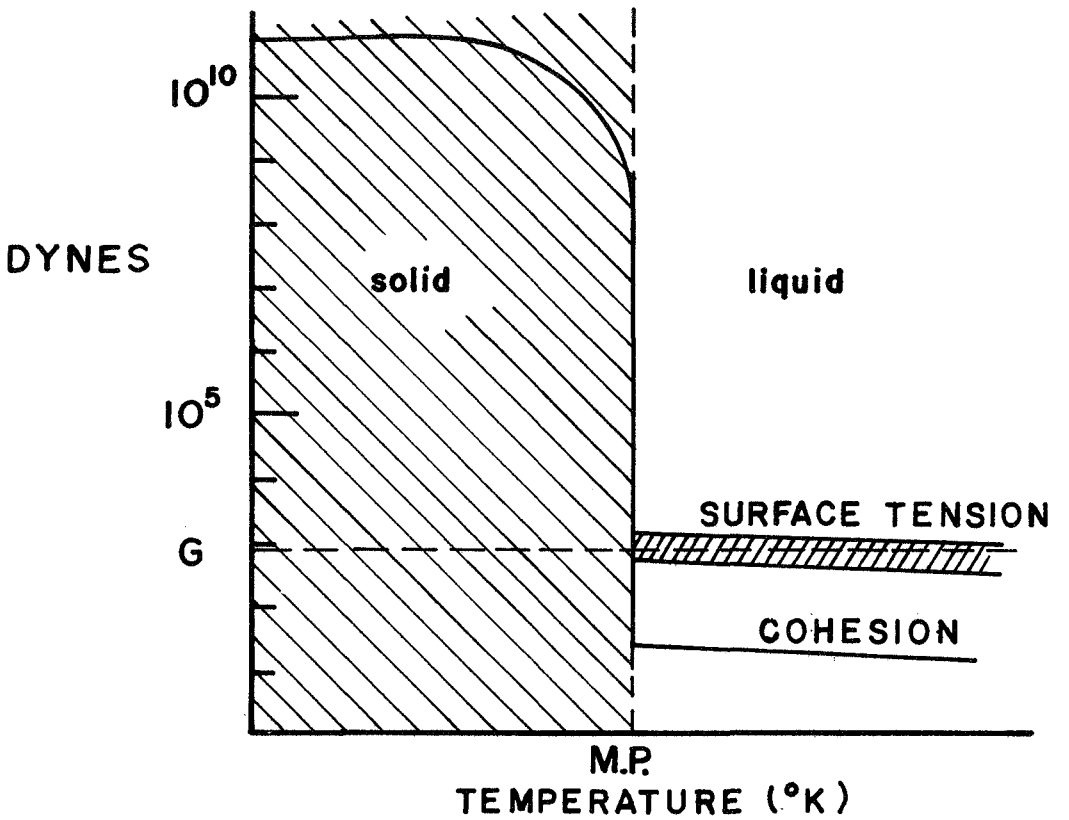

fig. I. INTERATOMIC FORCES OF MATTER

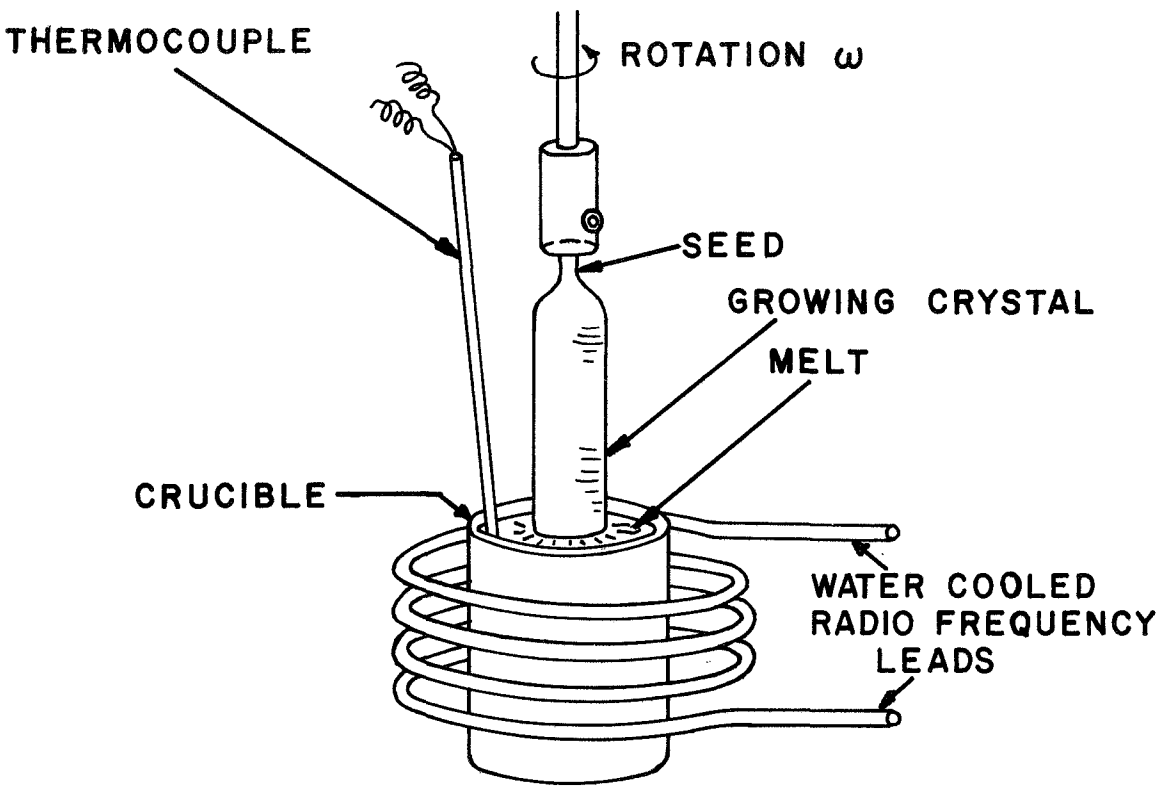

fig. 2 CZOCHRALSKI GROWTH
(schematic)

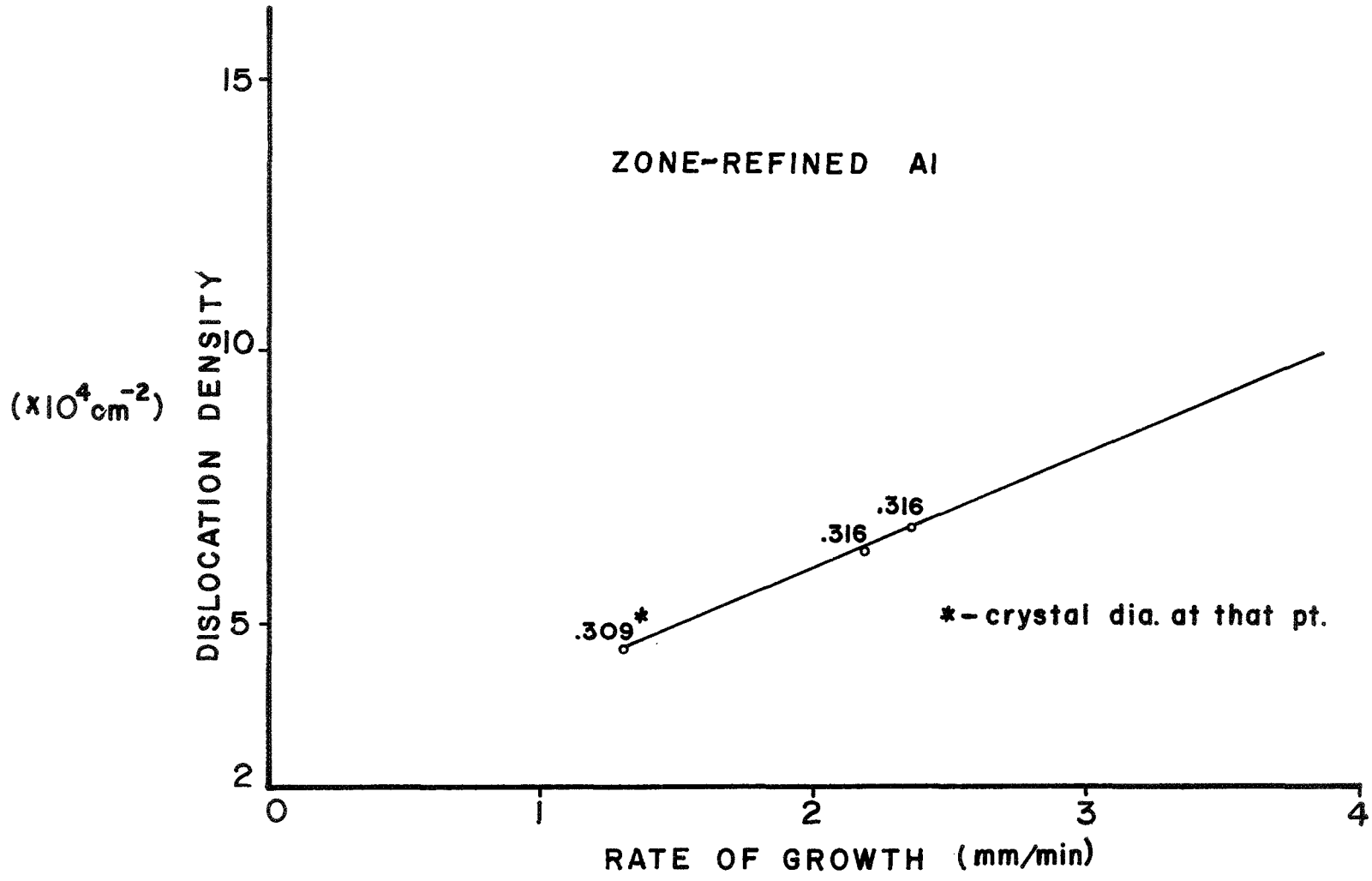

fig. 3. DISLOCATION DENSITY vs. GROWTH RATE

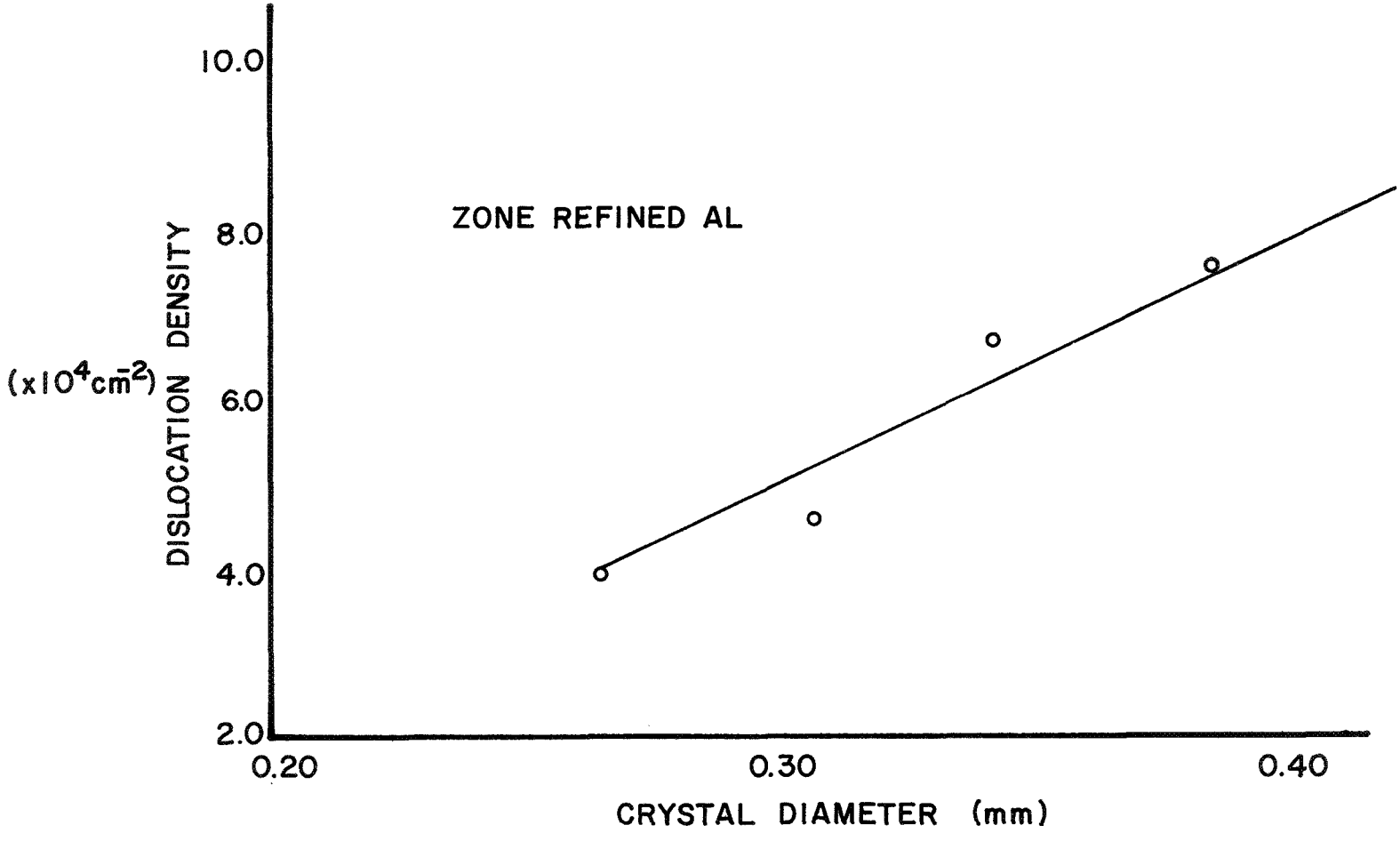

fig. 4 DISLOCATION DENSITY vs. CRYSTAL DIAMETER

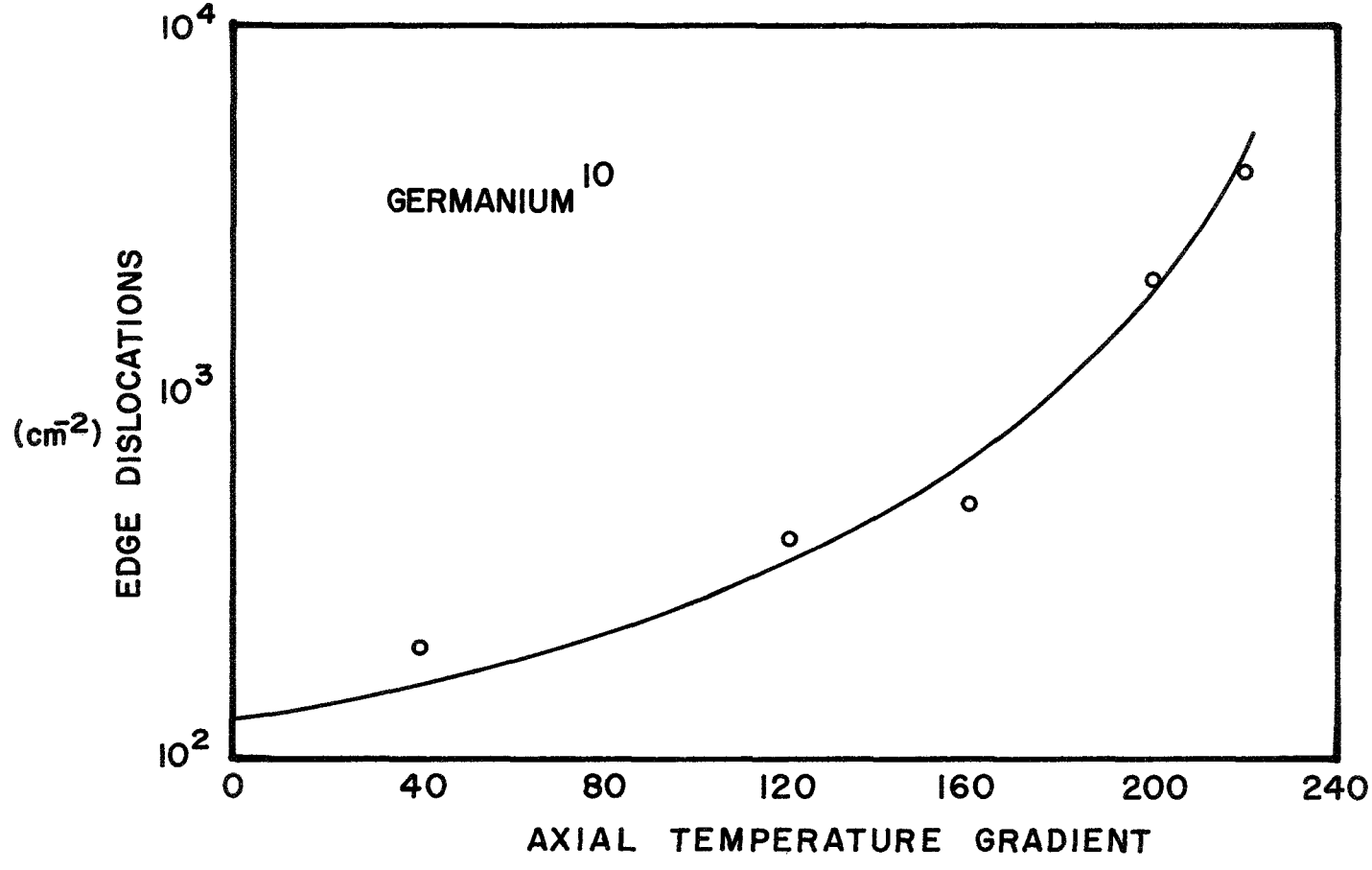

fig. 5 DISLOCATION DENSITY vs. AXIAL TEMPERATURE GRADIENT

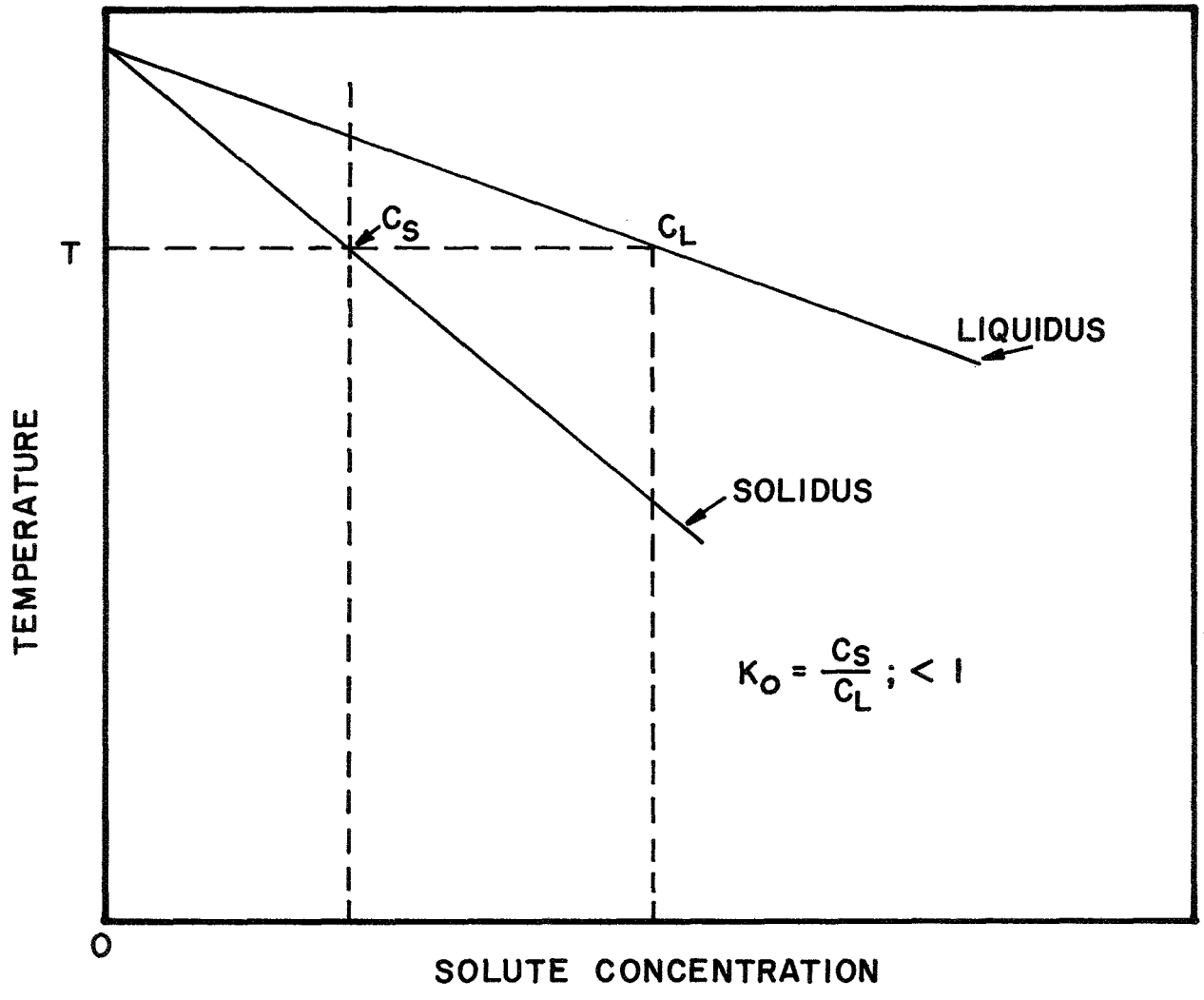

fig. 6 A SCHEMATIC TEMPERATURE - CONCENTRATION DIAGRAM

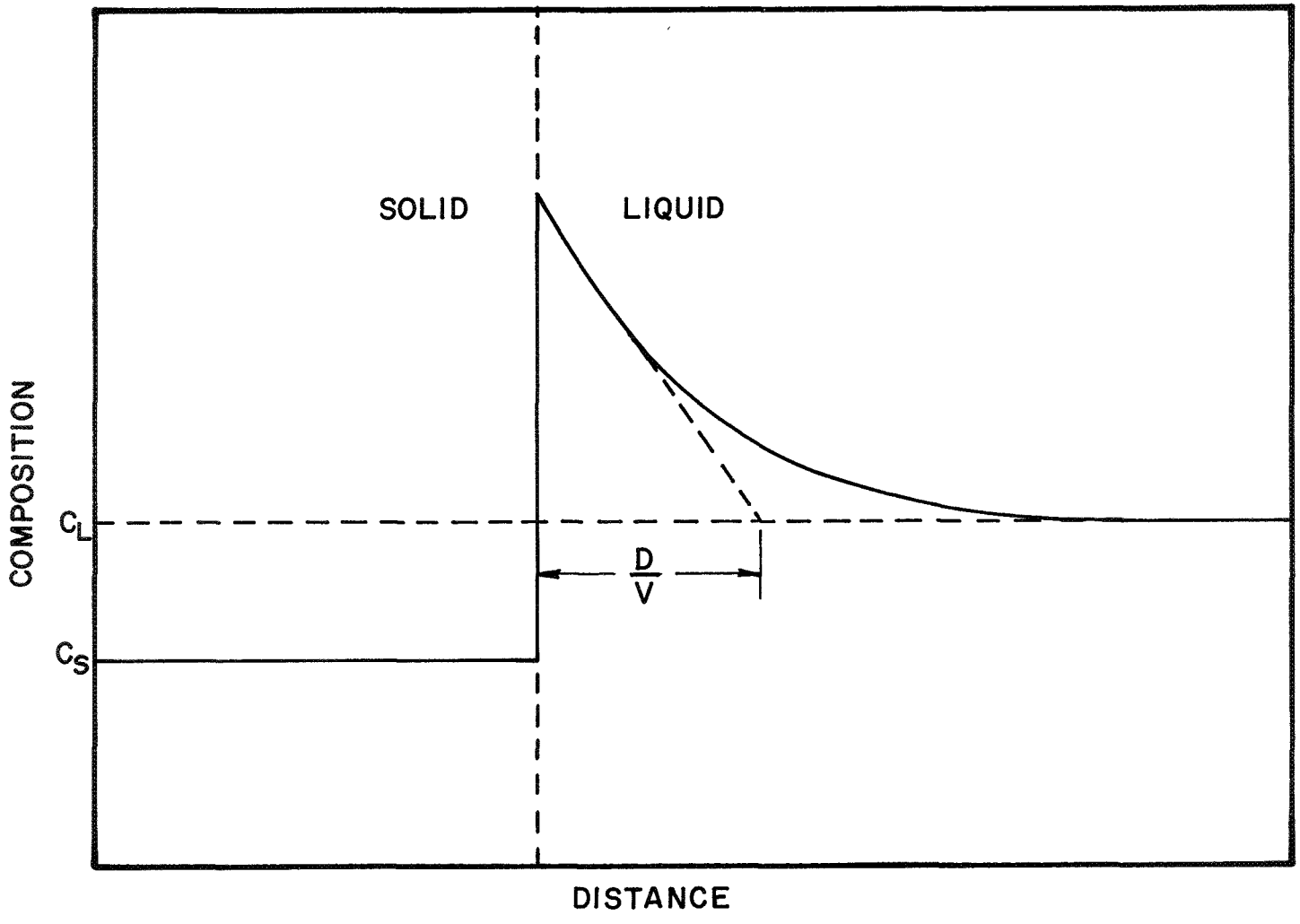

fig. 7 THE DIFFUSION BOUNDARY LAYER AHEAD OF A GROWTH FRONT

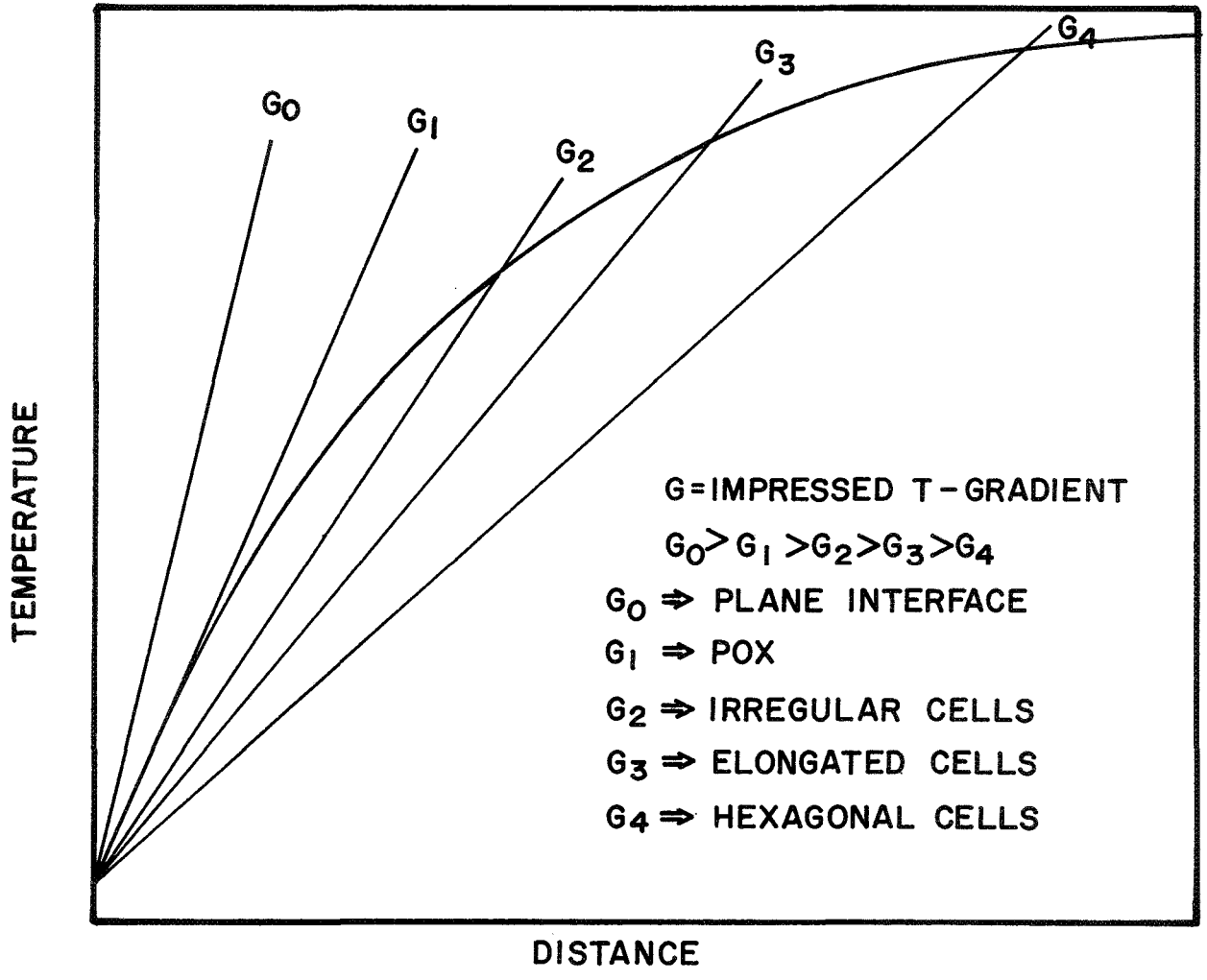

fig. 8 CONSTITUTIONAL SUPERCOOLING

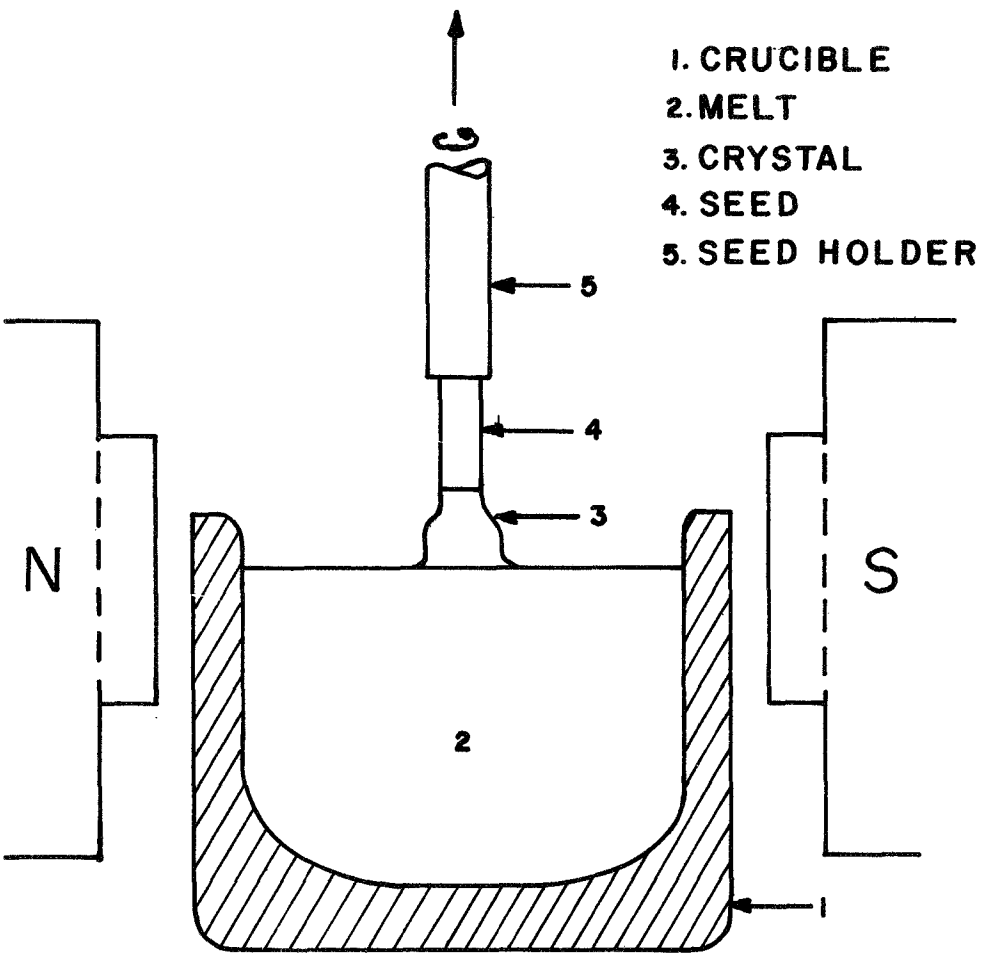

fig. 9. CRYSTAL GROWTH UNDER VARIOUS G-FIELDS

TABLE I. CANDIDATE SPACE PROCESSING MATERIALS

MATERIAL	MELTING POINT	CRYSTAL GROWTH TECHNIQUE	APPLICATIONS
Orthoferrite $TbFeO_3$	850°C	Flux Growth Hydrothermal	Memory Cores
Barium Sodium Niobate $Ba_2NaNb_5O_{15}$	~1500°C	Czochralski	SHG, Pyroelectric, and Memory
Linobate $LiNbO_3$	1260 ± 10°C Congruent Melting	Czochralski, Bridgeman, LiF—Flux	Electro-optic material, Piezoelectrics, acousto-optic modulators, transducers
Gallium Arsenide	1238°C (High as Vapor)	Czochralski, Bridgeman Horizontal Boat	Semiconductor devices, Laser, microwave devices
YIG $Y_3Fe_5O_{12}$	1560°C Incongruent Melting	Czochralski, Flux	Transducers, Laser Components
V_3Si	1950°C Congruent	Float Zone Melting	High Tc Superconductors
Organic Superconductors	------	------	Possibility of Room Temperature Superconductivity
Chlorpromazine	57°C	Zone-Refining	Tranquilizer